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Enthalpies of solution and enthalpies of solvation of chloro- and nitro-substituted benzenes in 1-butyl-3-methyl imidazolium based ionic liquids at 298.15 K: Additivity of group contributions

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ABSTRACT

In this work thermochemistry of solution and solvation of mono- and di-substituted chloro- and nitro-benzenes in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][TfO]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf2]) ionic liquids was studied. Enthalpies of solution at infinite dilution of benzene, chlorobenzene, nitrobenzene, 1,2-, 1,3-, 1,4-dichlorobenzenes, 1,2-, 1,3-, 1,4-dinitrobenzenes, 1-chloro-2-nitrobenzene, 1-chloro-3-nitrobenzene, and 1-chloro-4-nitrobenzene in three ionic liquids were measured at 298.15 K. On the basis of experimental data enthalpies of solvation of substituted benzenes in ionic solvents were calculated. Values of Cl and NO_2 group contributions to the enthalpies of solvation were derived and compared with molecular solvents. Enthalpies of solvation of each series of dichlorobenzenes, chloronitrobenzenes and dinitrobenzenes in studied ionic liquids are equal and do not depend on the mutual position of substituents. This fact shows that dipole moment does not affect the enthalpy of solvation of organic solutes in ionic liquids. Enthalpies of solvation of disubstituted benzenes in ionic liquids calculated through group contribution approach were in good agreement with experimental data.

1. Introduction

Ionic liquids are organic salts comprised of a bulky organic cation and coordinating organic or inorganic anion, which have melting temperature below than decomposition temperature. Nowadays interest in studies of ionic liquids is growing steadily due to a variety of their possible applications. The room temperature ionic liquids (RTILs) are most promising among them. These compounds have low vapor pressure, high thermal stability and can dissolve different types of solutes depending on combination of anion and cation structure. So, RTILs are good candidates for using as alternative "green solvents" and reaction media for synthesis, extraction and separation processes [1–4]. Thus, knowledge of physical-chemical properties of solutes dissolved in RTILs is crucial for application of ionic liquids as solvents. These properties significantly depend on intermolecular interactions in solution. At the same time intermolecular interactions are determined by the structure of solute and solvent molecules. Enthalpy of solvation presents the quantitative measure of solute-solvent interactions. This value can be used for analysis of solutions of ionic liquids and for extrapolation its properties to different temperatures through standard thermodynamic procedure. Enthalpies of solvation can not be measured experimentally, except gaseous solutes. For their determination we need to know enthalpy of solution and enthalpy of vaporization (liquid) or sublimation (solid) at the same temperature. Measurements of these values require special techniques, a sufficient amount of solute and solvent and a certain period of time. Even the fulfillment of all conditions does not guarantee reliable results. Therefore, different empirical approaches for predicting the enthalpy of solvation are in demand.

Part of these approaches is based on multi-parameter correlations, where each parameter is responsible for a special property of solute or solvent molecules (volume, polarity, basicity, acidity, etc.). Multi-parameter correlations were successfully applied for prediction of solvation enthalpies in molecular solvents [5,6]. Nowadays, one of the widely used of them is linear solvation energy relationship (LSER) approach proposed by Acree and Abraham [7]. This approach is based on multi-parameter correlations of solvation enthalpies and six solute descriptors [8–10]. These solute descriptors include hydrogen-bond acidity (A) and basicity (B), excess

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